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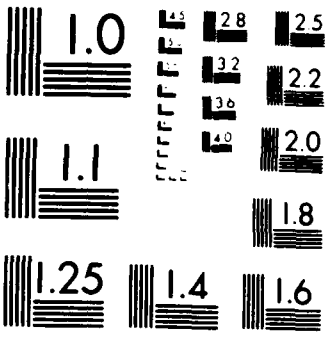

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STUDY OF BOUNDARY STRUCTURES

FINAL REPORT

RYOICHI KIKUCHI

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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The project extends ~~our~~ previous study on structures of a 2-D grain boundary (g.b.). Three major tasks have been done. The previous work in 1980, called A, was for a pure component system. In the work labeled B, impurities are added to the system and the adsorption of impurities at the g.b. is calculated. The work labeled C is closely tied to B and formulates atomic diffusion in a system with the g.b. The work labeled D is for a binary system of composition close to stoichiometry, which becomes ordered.

The CVM and PPM. The basic analytical tool is the cluster variation method (CVM) and the path probability method (PPM), both developed by the author. In the CVM, the free energy is minimized with respect to a large number of variables using a linear iteration method called the natural iteration method (NIM). These methods work nicely.

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The quadruple square (QS treatment. A square lattice is chosen as the basic lattice (called the DSC lattice) of the analysis. The first, second, and third nearest neighbor pairs are excluded due to a large repulsion. The fourth and fifth neighbors contribute interaction potentials $E_{4,AB}$ and $E_{5,AB}$, and so on. In the DSC lattice the CVM is formulated using a cluster made of nine lattice points in the form of a quadruple square. The QS formulation leads to numerical results that are reliable compared with the MC method.

The pair treatment. In low temperatures, atoms hardly deviate from the skeletal stable crystalline structure, and hence we can ignore DSC lattice points not on the stable crystal which is a square lattice. Then we can use the pair cluster as the basic cluster. The pair method is found to give reliable numerical results practically the same as those of QS for low temperatures including the entire ordered phase in the work D. This result is significant because when the pair method is used, the two sides of the g.b. do not need to be oriented symmetrically as were done in the present report. Applications of this point of view for g.b. of different angle combinations and the 3-D cases are now planned.

Hybrid cluster. In the work D for the ordered system g.b., it is found necessary to supplement the pair cluster by a triangle cluster near the coincident lattice site. Such a hybrid choice of clusters was tried for the first time, but it makes sense. We will need more hybrid choices near the g.b. center in order to take into account the frustration effect of atoms.

The low temperature "melting" of g.b. In all of A, B, and D cases, we found that the low T behavior and the high T behavior of g.b. can be clearly distinguished. In low T, it is crystal-like. As T increases, the g.b. opens up as $-\log (T_m - T)$, with T_m being the bulk melting temperature. The transition region between the two is about one-half of T_m.

Diffusion along the g.b. Diffusion along the g.b. is orders of magnitude larger near the g.b. than the bulk diffusion. The diffusion coefficient is proportional to the square of the local vacancy density. This holds when the impurities are adsorbed to the g.b. and also when they are repeated.

1. Introduction and Summary

In any type of crystalline materials, be it metallic, ceramic, dielectric, or semiconducting, grain boundaries (g.b.) play the key roll in affecting mechanical properties (strength and toughness). However, the atomic structure of g.b.has not been known, except the $T = 0$ behavior, mainly because of the lack of techniques which can analyze the structure. The present project studies the structure and properties of g.b. in a two-dimensional system for finite temperatures using statistical mechanical techniques developed by the author.

In one of the tasks performed under the contract preceding the present one, a 2-D grain boundary (g.b.) was studied theoretically.[1] The free energy F of the entire system (including the g.b.) was written in terms of the variables (called the state variables) which represent probabilities of local configurations. The special feature of this work was that the cluster variation method (CVM)[2] was used in formulating the entropy in terms of the basic variables. By minimizing F, the equilibrium state of the g.b. was derived, including the density profile and the excess free energy value. Since this work forms the basis of the tasks done under the contract being reported here, we attach Ref. 1 as Appendix A.

One of the main conclusions of Ref. 1 was that the g.b. starts to melt at around one-half of the melting temperature T_m, and the g.b. broadens near T_m as $-\log(T_m - T)$. This conclusion attracted the interest of workers and several papers have been published on the subject reporting the Monte Carlo simulations. The low temperature g.b. melting was confirmed by the simulations, the latest paper of which may be the one due to Yip et al.[3]

Since the method used in Ref. 1 is versatile in studying properties of grain boundaries, we extended it to several cases during the present contract. The results are in Appendices B, C, and D, and they are summarized in subsequent sections.

Appendix B is an extension of Ref. 1 and includes impurities. Appendix C is based on B and calculates atomic diffusion along the g.b. This paper is significant in that the technique of irreversible

statistical mechanics (the path probability method[4] PPM) is used in the g.b. studies. It is shown that diffusion is orders of magnitude larger near the g.b. compared with the bulk diffusion. One significant result is that for either case when the impurities are adsorbed to or rejected from the g.b., the diffusion coefficient becomes large near the g.b. in proportion to the square of the local vacancy concentrations.

Appendix D works with the g.b. between two ordered phases. The symmetric boundary and asymmetric boundary are distinguished. The profile of the long-range order across the g.b. is calculated.

In the boundary problems the number of independent variables is usually large, easily exceeding 1000, and a minimum of the free energy (actually the grand potential Ω) is to be found with respect to these variables. The linear iteration technique called the NIM[5] works amazingly well and Ω always decreases as the iteration proceeds, however small the decrement may be.

The importance of the grain boundaries in influencing mechanical properties of materials comes mainly from the concentration of vacancies at the g.b. Statistical mechanics can calculate the amount of vacancies at the g.b. as we have done in this project and reported in the appendices. The concentration of vacancies, however, is only the beginning of the g.b. studies of practical importance. It is needed to proceed to study *how the vacancies influence kinetic behavior of the materials.*

The diffusion study in Appendix C is one step ahead of the prevailing effort of statistical mechanics, but still is far short of the really important aspect of the kinetic study, namely the plastic deformation and fracture. It is planned that we will move on to the study of grain boundary contribution to these phenomena.

The CVM and PPM are very well suited in studying the structure of boundaries analytically. Although the way may still be long to achieve the goal of understanding mechanical properties of materials from microscopic behavior, we will continue our effort towards the goal by improving these methods.

2. Grain boundaries with impurities in a two-dimensional lattice gas model (attached as Appendix B)

The model of Ref. 1 was extended to include impurities. The work was accepted for publication in Physical Review B, and is attached as Appendix B in this report. The g.b. is formed on the basic DSC lattice. In the CVM analysis we use a quadruple square (QS) of nine DSC points as the basic cluster.

When the matrix-impurity interaction is repulsive so that the impurities are rejected from the bulk matrix, they are adsorbed near the grain boundary. This is because vacancies are concentrated around the g.b. When the matrix and impurity interaction is attractive, impurities stay away from the g.b. The amount of adsorption is calculated as a function of temperature.

As was observed in Ref. 1, the low temperature structure and the high temperature structure of the g.b. can be clearly distinguished. In the high temperature region, the g.b. widens as in Ref. 1, depending on T as $-\log(T_m - T)$. This behavior is derived based on the calculations of both the entropy and the adsorption.

3. Theory of diffusion along a 2-D grain boundary (attached as Appendix C)

The papers published so far in this and preceding ARO contracts are all based on the cluster variation method (CVM)[2,5] of equilibrium statistical mechanics. The basic approach is to minimize the free energy (actually the grand potential) with respect to the basic variables to derive the equilibrium state.

The CVM has been extended to non-equilibrium processes by treating the time axis as the fourth space axis. The extension has been called the path probability method (PPM).[4] It was used successfully in treating atomic diffusion in crystals[6,7], and in the kinetics of phase transitions.[8]

In the attached Appendix C, we have used the PPM to study atomic diffusion along a grain boundary. A chemical potential gradient $\vec{\nabla}\mu$ is imposed along the g.b. to induce atomic flux. Qualitatively speaking, the ratio of the flux and $\vec{\nabla}\mu$ gives the diffusion coefficient. The treatment is based on the equilibrium formulation in Appendix B and works on the impurity g.b. case.

Taking advantage of the finding in the following section 4, the diffusion is formulated in the skeletal crystalline lattice only (ignoring the rest of the DSC lattice points) using the pair as the basic cluster. This is drastically simpler than using a nine point QS as the basic cluster of the diffusion formulation.

The work has a novel technical contribution. In previous PPM formulations[6,7] of diffusion, only the bulk diffusion was treated, and thus the gradients of state variables are small under the imposed $\vec{\nabla}\mu$. In the present case, the gradients of states variables are not small near the g.b. It is shown in Appendix C that even when the space gradients of state variables in equilibrium are large, atomic fluxes can be formulated when small $\vec{\nabla}\mu$'s are imposed.

When a reasonable set of kinetic parameters are used, numerical computations lead to the results that the diffusion is many orders of magnitude faster near the g.b. than inside the bulk. This result holds even when the impurities are adsorbed to or repelled from the boundary. The diffusion coefficient is roughly proportional to the square of the local vacancy concentration.

The diffusion coefficient along a line parallel to the g.b. follows the Arrhenius relation nicely, and the activation energy can be determined for each line at a certain distance from the g.b. The activation energy is smaller near the g.b., corresponding to the accumulation of vacancies near the g.b. center.

4. 2-D grain boundary between ordered phases (attached as Appendix D)

Extending the work in Appendix B, a 2-D g.b. between two ordered phases is studied. The DSC lattice of Appendices A and B form the basis of the analysis, and the stable crystalline state is the square lattice of the same shape. In this paper, the skeletal square lattice is ordered when the system is close to the stoichiometric AB alloy.

Two approaches were used in the formulation. One is based on the DSC and uses the quadruple square (QS) mentioned in Section 2 as the basic cluster. The other works only with the skeletal square lattice and uses a pair of lattice points in this lattice as the basic cluster. A significant finding is that the two approaches give identical numerical results for low temperatures including the entire ordered region.

For the coherent boundary of the present study, the symmetric boundary and the asymmetric boundary are distinguished. Under a certain choice of interaction parameters, the stable boundary is symmetric in low temperatures but switches to asymmetric in high temperatures.

The bulk shape of the skeletal crystalline lattice is the square lattice. However, near the g.b. the shape is distorted and thus the pair cluster is insufficient in taking into account the frustration effect. It was found that an additional triangle cluster near the coincidence lattice site can remedy the entropy expression and leads to the correct kln2 value at the 0K limit.

5. Transition layer in a lattice-gas model of a solid-melt interface (attached as Appendix E)

The analysis of IPB's between the Cu-Au phase and the disordered phase [illegible] period can be interpreted as a model of a solid-melt interface. Based on [illegible] deduce that perpendicular to densely packed planes a crystal [illegible] into the melt, while perpendicular to less densely packed planes crystalline [illegible] melt. This result is in agreement with computer simulations.

Appendices A through E

[illegible] this final report, it was decided not to attach the [illegible] because further delay of the report, we decided to [illegible] only their names and references. However, [illegible] Appendices A through E are available for [illegible].

Appendix A: [illegible] two-dimensional lattice-gas model," by R. [illegible] Phys. Rev. B [illegible].

Appendix B: [illegible] three-dimensional lattice-gas model," by R. Kikuchi [illegible].

Appendix C: [illegible] Domain Boundary," by P. Cendese and R. Kikuchi.

Appendix D: [illegible] and Real Phases," by P. Cendese and R. Kikuchi.

Appendix E: "Correction Energy in a Lattice-gas model of a solid-melt interface," by J.W. Cahn and R. Kikuchi, Phys. Rev. B31 (1985), 4300.

Appendix F: Comprehensive summaries of Kikuchi's work on boundary structure related to the present contract.

Appendix F

Complete summary of the author's work on boundary structure related to the present contract.

Since the present final report closes the series of projects on boundary structure supported by the U.S. Army Research Office, and a new page of the boundary studies is about to open, it is appropriate to summarize the entire work done by the author in the subject of interest.

1. CVM and PPM

These two methods form the basis of the boundary studies.

(K51) R. Kikuchi, "A theory of cooperative phenomena," Phys. Rev. 81 (1951) 988. This is the first full paper on the CVM, and is still a good introduction.

(KB67) R. Kikuchi and S.G. Brush, "Improvement of the cluster-variation method," J. Chem Phys. 47 (1967) 195. For a 2-D systm, 1-D long clusters are enough to obtain good accuracy.

(K74) R. Kikuchi, "Superposition approximation and natural iteration calculation in cluster-variation method," J. Chem. Phys. 60 (1974) 1071. The NI method is an important computational device to use in the CVM.

(K66) R. Kikuchi, "The path probability method," Prog. Theor. Phys., Suppl. No. 35, p. 1 (1966). Still a good introduction to the PPM.

2. Early papers

(K60) R. Kikuchi, "Statistical dynamics of boundary motion," Annals of Phys. 11 (1969 328. This is the first paper by the author on the boundary structure. It is interesting that the work was on kinetics. The Ising model boundary between the + and − domains is moved perpendicular to itself under an external magnetic field. The velocity of the motion is derived as an eigenvalue of a differential equation. The formulation was done using the point approximation of the PPM.

(CK61) J.W. Cahn and R. Kikuchi, "Theory of domain walls in ordered structures I. Properties at absolute zero," J. Phys. Chem. Solids 20 (1961) 94.

(KC62) R. Kikuchi and J.W Cahn, "Theory of domain walls in ordered structures II. Pair approximation for nonzero temperatures," J. Phys. Chem Solids 23 (1962) 137.

(CK66) J.W Cahn and R. Kikuchi, "Theory of domain walls in ordered structures III. Effect of sutstitutional deviations from stoichiometry," J. Phys. Chem. Solids 27 (1966) 1305. In these three papers, the CVM was used. *However, since the NI method in* (K74) below was not known, only the pair approximation was applied for an antiphase boundary (APB) in bcc.

3. The scalar product (SP) formulation

The excess free energy of the boundary is calculated using only the bulk properties of the two sides.

(K67) R. Kikuchi, "Cooperative phenomena in the triangular lattice," J. Chem. Phys. 47 (1967) 1664. This paper shows that the "central hump" of the free energy curve disappears as we improve approximation in the CVM hierarchy. This conclusion makes us question the validity and/or accuracy of the CVM treatments of the boundary structure, for example in the papers in 2 above.

(CW71)D.B. Clayton and G.W. Woodbury, Jr., J. Chem. Phys. 55 (1971) 3895. This paper shows how to calculate the excess free energy of a boundary using the bulk properties only of the two sites. Their method is used in the subsequent papers.

(K72I,II,III) R. Kikuchi, "Boundary free energy in the lattice model. I. General formulation," J. Chem. Phys. 57 (1972) 777; "II. Applications of the general formula," J. Chem. Phys. 57 (1972) 783; "III. Solution of the paradox," J. Chem. Phys. 57 (1972) 787. These three papers present detailed discussions of the SP method, and the interpretation of the CVM treatment in 2.

(K72IV) R. Kikuchi, "Phase transition within a phase boundary," J. Chem. Phys. 57 (1972) 4633. Using the SP method, it is shown that an order-disorder type phase transition occurs within a phase boundary, when the boundary itself is 2-D.

(K73) R. Kikuchi, "Phase transition within a phase boundary II," Scripta Met 7 (1973) 275. This compares works of several different groups on the subject.

(K76) R. Kikuchi, "Natural iteration method and boundary free energy," J. Chem. Phys. 65 (2976) 4545. From this paper on, the boundary work was supported by the U.S. Army Research Office. The paper uses the NI method to calculate the boundary free energy formulated by the SP method.

(K77a) R. Kikuchi, "The scalar-product experssion of boundary free energy for long-range interacting systems," J. Chem. Phys. 68 (1977) 119. The SP formulation is extended to the case when the interaction is not limited to the nearest-neighbor pairs.

4. Introduction of the NIM

The natural iteration method (NIM) was devised in (K74) quoted in 1 above. The NIM made it possible to calculate boundary structure with basic clusters larger than the pair.

(K77b) R. Kikuchi, "Structure of phase boundaries," J. Chem. Phys. 66 (1977) 3352. In addition to the NIM, a special technique adopted from the work of Weeks and Gilmer is used to calculate $<110>$ boundary of the bcc Ising model using a tetrahedron as the basic cluster. Results are compared with the SP treatment of the same boundary.

5. Fcc boundary (IPB and APB) using a tetrahedron

(CK79) J.W. Cahn and R. Kikuchi, "Ground state of fcc alloys with multiatom interactions," Acta Met. 27 (1979) 1329.

(KC79) R. Kikuchi and J.W. Cahn, "Theory of interphase and antiphaes boundaries in fcc alloys," Acta Met. 27 (1979) 1337. These two papers form a connected pair. IPB and APB of Cu_3Au are calculated using the tetrahedron as the cluster. The bulk phase is the best analytical formulation calculated by van Baal, Golosov, Kikuchi, and de Fontaine using the CVM.

(CK85) J.W. Cahn and R. Kikuchi, "Transition layer in a lattice-gas model of a solid-melt interface," Phys. Rev. B31 (1985) 4300. This is the paper in Appendix E of this report.

6. 2-D grain boundary studies.

This is the last category of the boundary studies done by the author so far. The papers are in Appendices A through D of this report.

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8. K. Gschwend, H. Sato, and R. Kikuchi, "Kinetics of order-disorder transformations in alloys. II", J. Chem. Phys. **69** (1978) p. 5006.
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